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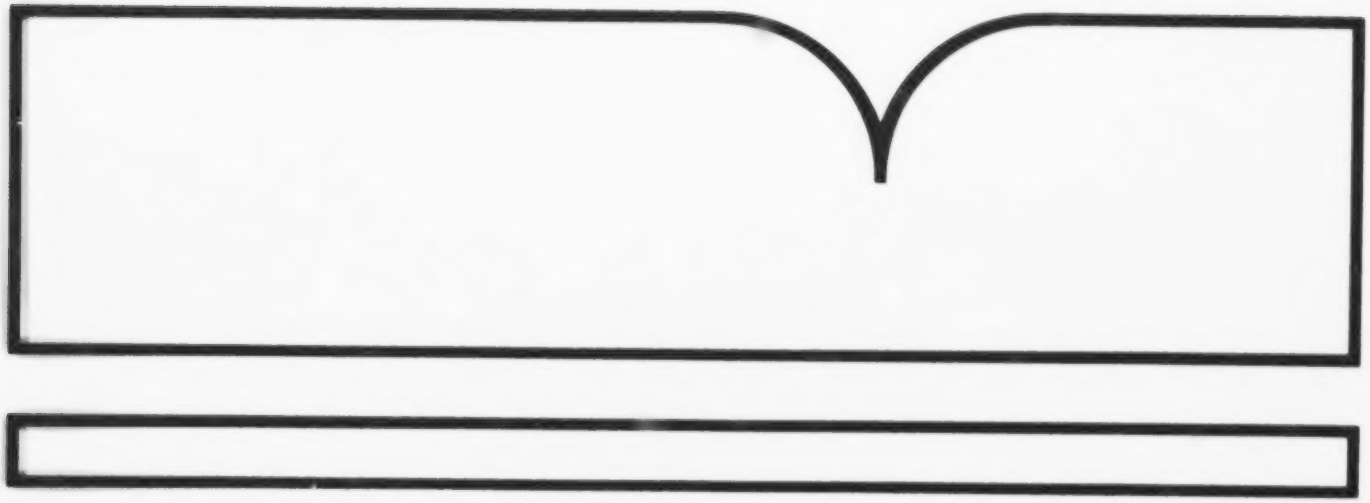

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STRUCTURE-REACTIVITY RELATIONSHIPS FOR PREDICTING ENVIRONMENTALLY HAZARDOUS CHEMICALS

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A method for extrapolating rate coefficients using transition-state theory was applied to reactions of hydroxyl (OH) radicals with 10 halomethanes and 18 haloethanes. The entropy of activation $\Delta S^{\pm}$ was calculated for each compound and together with an experimental value of the rate of reaction at 298 K was used to calculate k(T) at higher temperatures. The calculated values for all the haloalkanes differed from experimental values by no more than 25%, except that of $OH + CHCl_3$. A simpler scheme was developed for all haloalkanes for α-hydrogen abstraction $\Delta S^{\pm}(298) = -2.2 \ln M - 18.0 + R \ln n_H$ and the activation energy at 298K by $E(298)/R = 2100 - 85n_F - 51n_{Cl} - 950n_{CH_3} - 600nCH_2X - 650n_{CHX_2} - 250n_{CX_3}$

These two relations for $\Delta S^{\pm}(298)$ and E(298) were used to generate a "universal" rate coefficient expression that depends only on the molecular weight and the number of abstractable H atoms in the reagent haloalkane: $k(T) = n_H 10^{6.5} M^{-1} T^{1.5} \exp[-[E(298)/R-450]/T]$ where E(298)/R is given by the preceding equation. For most haloalkanes this expression predicts rate coefficients within a factor of 3 of experimental data and provides a useful predictive tool if no reliable data are available.

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ABSTRACT

A method previously developed for extrapolating rate coefficients by conventional transition-state theory was applied to reactions of hydroxyl (OH) radicals with 10 halomethanes and 18 haloethanes. For each reagent, the entropy of activation $\Delta S^{\ddagger}$ was calculated. That value, together with an experimental value of the rate of reaction at 298 K, k(298), was used to calculate k(T) at higher temperatures. The calculated values for all the haloalkanes differed from experimental values by no more than 25%, except that of ($OH + CHCl_3$), for which the possibility of experimental errors was considered.

Those calculations were then used to develop a simpler, approximate scheme that can be applied to any haloalkane. For α-hydrogen abstraction reactions, $\Delta S^{\ddagger}(298)$ can be fitted, with a maximum error of 1.4 and an average error of 0.3 cal mol^{-1} K^{-1} (entropy units, or eu), by

$$\Delta S^{\ddagger}(298) = -2.2 \ln M - 18.0 + R \ln n_H$$

where M = molecular weight of the haloalkane and n_H = the number of abstractable α-hydrogen atoms. The activation energy at 298 K, E(298), can be fitted, with an average error of 0.3 and a maximum error of 1.1 kcal/mol, by

$$E(298)/R = 2100 - 85n_F - 51n_{Cl} - 950n_{CH_3} - 600n_{CH_2X} - 650n_{CHX_2} - 250n_{CX_3}$$

where the n_i indicate the number of H atoms on CH_4 replaced with the indicated substituents, and X is either Cl or F. These two relations for $\Delta S^{\ddagger}(298)$ and E(298) were used to generate a "universal" rate coefficient expression that depends only on the molecular weight and the number of abstractable H atoms in the reagent haloalkane:

$$k(T) = n_H \, 10^{6.5} \, M^{-1} \, T^{1.5} \exp[-[E(298)/R-450]/T]$$

where E(298)/R is given by the preceding equation. For most reagents, this expression predicts rate coefficients within a factor of 3 of experimental data and provides a useful predictive tool if no reliable data are available.

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SECTION 1

INTRODUCTION

The aim of this research has been to develop the means for predicting reactivities of potential man-made pollutants in the stratosphere and troposphere. Although it is possible to measure reactivities in the laboratory, the number of possible species of concern is enormous, and the cost of studying each one in detail would be prohibitive. The assessment of the atmospheric fate of pollutant can, for the most part, be satisfied by a procedure that enables prediction of reactivities to within a factor of 3 to 5, without requiring the higher accuracy attainable by elaborate laboratory measurements.

In general, the reactive species in the atmosphere that will attack emissions from ground or airborne sources, with typical concentrations at 20 km altitude, are:

Species	Concentration (molecules/cm^3)	Concentration relative to OH
H	5×10^5	0.35
$O(^3P)$	1×10^6	0.7
OH	1.4×10^6	1.0
HONO	1.8×10^7	12
HO_2	3.5×10^7	25
H_2O_2	1.0×10^9	700
HNO_3	7.0×10^9	5000
NO_x	1.0×10^{10}	7000

Of these species, hydroxyl (OH) is almost always the most reactive with any given molecular substrate. Although all but hydrogen (H) and oxygen (O) are present in the atmosphere at concentrations exceeding that of OH, most have lower specific reactivities, so that OH is one of the most effective atmospheric oxidants. Consequently, any research concerned with predicting

lifetimes of potential pollutants should concern itself first with the reactions of OH radicals. For this reason, the work under this contract has focused on OH reactions. (Species concentrations closer to ground level may be somewhat different, but the conclusions are the same.) Our initial efforts proceeded in two phases: The first addressed the problem of calculating in detail the temperature dependence of the reaction rate coefficients; the second explored the possibility of developing simplified procedures for estimating with sufficient accuracy the rate coefficients of OH reactions at any temperature. The second phase required being able to estimate both the entropy of activation ($\Delta S^{\ddagger}$), and, with more difficulty, the energy of activation (E). These two parameters determine the rate of reaction at any temperature, in accordance with the general equation

$$k(T) = C \exp(\Delta S^{\ddagger}/R) \exp(-E_a/RT) \qquad (1)$$

Finally, we addressed the problem of developing a universal rate coefficient expression that can predict with reliability the rate coefficients, at various temperatures, for reactions of OH radicals with important atmospheric pollutants. Progress on these efforts is summarized briefly in Section 3.

SECTION 2

CONCLUSIONS

Four principal conclusions emerge from the present study. The first is that a reasonable set of assumptions can be applied consistently to all but one of the reactions considered here to obtain transition-state models that lead to calculated rate coefficients in good agreement with experimental data. This is true even though the A factors at 298 K are not in particularly good agreement with experimental values, as Jeong and Kaufman[1] found. The good agreement is a result of the tendency of activation entropies and energies to compensate one another.

The second conclusion is that one of the reactions--that of ($OH + CHCl_3$)--is anomalous. Either the experimental data are flawed or there is something unusual about the dynamics of this reaction, requiring a qualitatively different activated complex to obtain agreement between calculations and experiments. A new experimental investigation is recommended.

Third, the first two conclusions together demonstrate that, while one might be able to tailor a model for the activated complex to force reasonable agreement with a particular set of experimental data for one reaction, simultaneous agreement with data for several homologous reactions is by no means a fortuitous achievement. The greater constraints imposed by treating an entire family of reactions together rather than a single reaction give greater confidence that the model and the resulting calculations are physically meaningful.

Finally, we used the calculations just discussed as a guide for generating empirical expressions for $\Delta S^{\ddagger}(298)$ and $E(298)$ for α-hydrogen abstraction reactions of OH radicals from fluorinated and chlorinated methanes and ethanes. The calculated entropies and energies of activation were then used to generate a "universal" rate coefficient that depends only on the molecular weight and the number of abstractable α-hydrogen atoms of the reagent haloalkane. This expression predicts rate coefficients within a factor of about 3 of the experimental data for all 26 reactions for which data

were available (and generally much better), and holds a promise of being a predictive tool when no reliable experimental data are available.

SECTION 3

SUMMARY OF RESULTS

TRANSITION-STATE THEORY CALCULATIONS

In recent years, we have developed procedures for the use of transition-state theory to extrapolate, to arbitrary temperatures, rate coefficients for bimolecular reactions from one reliable experimental measurement. In essence, this procedure involves calculating the activation entropy for the reaction. Initial applications of this work were to reactions of OH and O atoms with alkanes. These past 3 years, with EPA support, we have extended our previous work to reactions of OH with halogenated alkanes, a family of compounds that includes many important atmospheric pollutants.

Under this EPA grant, we studied all reactions of OH radicals with halogenated alkanes for which reliable data were available. In the first phase, we examined nine chlorinated and fluorinated methanes. For eight of these compounds (CH_3F, CH_2F_2, CHF_3, CH_3Cl, CH_2Cl_2, CH_2ClF, $CHCl_2F$, $CHClF_2$) our predicted rate coefficient extrapolations were in good agreement (within a factor of 2 up to 500 K) with experimental data. However, for the ninth, $CHCl_3$, a serious discrepancy arose; either the model is inapplicable to this molecule for some inexplicable reason, or, more probable, there are errors in the experimental data. The measurements for $CHCl_3$ should be repeated in the laboratory to verify or refute our contention. If the calculations prove correct, this will be an important example of the use of transition-state theory as an independent means of judging the reliability of experimental data.

To extend the data base for halogenated alkanes, we carried out a series of calculations on several halogenated ethanes. The model proved as successful for these compounds as it was for the halomethanes, thus giving us confidence that we have a general procedure that can be used for all halogenated alkanes. This effort, combined with our previous work on (OH + alkanes) and (O + alkanes), provided useful general insights into the practical problems of predicting activation entropies for a broad range of bimolecular metathesis (i.e., of the form A + BC = AB + C) reactions.

ACTIVATION ENTROPIES

With these detailed transition-state theory calculations for halomethanes and haloethanes to guide us, we next examined the problem of developing a simpler, approximate scheme for predicting the activation entropy of a reaction of OH with an arbitrary haloalkane without going through the detailed calculations. We observed that the activation entropy seemed to correlate well with the molecular weight of the reacting haloalkane. A least-squares fit through all our calculated data gave a fairly good fit, for α-hydrogen abstractions, in the form

$$\Delta S^{\ddagger}(298) = -2.2 \ln M - 18.0 + R \ln n_H \qquad (2)$$

where n_H is the number of α-hydrogen atoms. Details are given in Section 4.

ACTIVATION ENERGIES

The goals of this project included not only rate coefficient extrapolation, but rate coefficient estimation when no data at any temperature were available. The latter requires predicting the activation energy as well as the activation entropy, a more difficult task at present. Currently, there are a priori theoretical procedures for calculating the energies of activation within 2 to 3 kcal/mol. The procedures are costly and time-consuming, even on the current generation of supercomputers. Unfortunately, an error of 2 kcal/mol in the activation energy produces an error of a factor of 30 in a room-temperature rate coefficient, which is unacceptably large for research needs. Consequently, we looked to semiempirical methods of estimation based on existing data for analogous reactions.

There have been previous published attempts at correlating reaction rate coefficients with bond dissociation energies. Some of these give good correlations for large classes of reactions, predicting rate coefficients to within a factor of 3 to 5 at room temperature. However, correlations between rate coefficients and bond dissociation energies will always be limited because they are, in effect, correlating activation energies and activation entropies simultaneously with the same molecular properties. Because we have good techniques for calculating activation entropies, we preferred to

correlate just the activation energies with bond dissociation energies. With the complete halomethane/haloethane series of reactions as a data base, we explored a simple empirical procedure for estimating activation energies. The procedure begins from the known activation energy for the reaction of OH with CH_4. It is then assumed that, for each H atom replaced by a Cl, F, CH_3, CH_2X, CHX_2, or CX_3 group, where X = F or Cl, there is a well-defined correction term added to or subtracted from the CH_4 activation energy to obtain the activation energy of the substituted compound. For example, suppose we wish to predict the activation energy for the OH abstraction of an H atom from the possible pollutant CHF_2CCl_3. We begin with the general equation

$$E(RH) = R(CH_4) - a_F n_F - a_{Cl} n_{Cl} - a_{CH_3} n_{CH_3} - a_{CH_2X} n_{CH_2X} - a_{CHX_2} n_{CHX_2} - a_{CX_3} n_{CX_3} \quad (3)$$

where the a_i are constants determined by a best fit to the experimental data available for all the compounds, and the n_i indicate the number of the substituents in the molecule of interest. (For the values of the derived a_i, see the following sections.) For CHF_2CCl_3, $n_F = 2$ and $n_{CX_3} = 1$. Therefore,

$$E(CHF_2CCl_3) = E(CH_4) - 2a_F - a_{CX_3}$$

If the data base were larger, separate terms could be developed for CCl_3, CF_3, etc. Data are at present insufficient to include brominated compounds in this formulation.

UNIVERSAL RATE COEFFICIENT

It is possible to generate a "universal" rate coefficient expression that depends only on the molecular weight and the number of abstractable H atoms in the reagent haloalkane by substituting Eqs. (2) and (3) in Eq. (1) and forcing the exponent of T to be 1.5, in agreement with transition-state theory calculations:

$$k(T) = n_H \, 10^{6.5} \, M^{-1} \, T^{1.5} \, \exp[-[E(298)/R-450]/T] \quad (4)$$

where n_H is the number of α-hydrogen atoms, M is the molecular weight of the haloalkane in daltons, T is the temperature in kelvins, and k(T) is the temperature-dependent rate coefficient in L mol^{-1} s^{-1}.

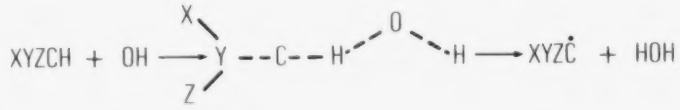
In the following sections are given the details of this formulation and the results. We consider the approach quite successful: For all but 2 of the 28 halomethanes and haloethanes for which data were available, this procedure predicted rate coefficients within a factor of 3 of the experimental data. It thus holds the promise of being a predictive tool when no reliable data of any sort are available.

SECTION 4

PROCEDURE

TRANSITION-STATE THEORY CALCULATIONS

Our procedure is basically the same as in our previous studies.[2,3] Here the general reaction is



where X, Y, and Z are each either H, Cl, F, CH_3, or a halomethyl radical. The principal problem is how to calculate the entropy of the activated complex, $S^{\ddagger}$. Our approach is to use the haloalkane reagent itself as a model compound, then make corrections to the various degrees of freedom as indicated below. This approach differs from that of another recent study,[1] in which the halogenated alcohols were used as model compounds. We prefer the reagents as models because the entropies of the corresponding alcohols are not known, and estimating them introduces other, unnecessary, opportunities for errors. $S^{\ddagger}$ is then given by

$$S^{\ddagger} = S^{0}_{RH} + \Delta S_t + \Delta S_v + \Delta S_r + \Delta S_{ir} + \Delta S_e + \Delta S_\sigma + \Delta S_n \qquad (5)$$

where the ΔS terms represent the corrections required to replace the properties (translation, vibration, rotation, internal rotation, electronic, symmetry, optical isomerism, respectively) of the model compound by those of the activated complex.

We assume that the C·H , H·O, and O-H bond lengths and C·H·O and H·O-H bond angles are approximately the same as those calculated by Walch and Dunning[4] for the reaction of ($OH + CH_4$): 1.2, 1.3, 1.0 Å and 160° and 110°, respectively. From this information the product of moments of inertia of the complex, $I^{\ddagger}$, can be calculated, whence $\Delta S_r = R \ln(I^{\ddagger}/I)$, where I is the product of the moments of inertia of the reagent RH. ΔS_t is given by (3/2) R × $\ln(M^{\ddagger}/M)$. The electronic degeneracy of the activated complex is assumed to

be 2, whence $\Delta S_e = R \ln 2 = 1.38$ eu (entropy units, or cal mol^{-1} K^{-1}). $\Delta S_\sigma = R \ln(\sigma/\sigma^\ddagger)$, where σ and $\sigma^\ddagger$ are the external symmetry numbers of the alkane and complex, respectively, calculated assuming rigid rotation. $\Delta S_n = R \ln (n^\ddagger/n)$, where n and $n^\ddagger$ are the numbers of optical isomers in the alkane and complex, respectively. Only the vibrational frequencies and internal rotations of the activated complex remain to be determined.

Vibrational Frequencies

For each halomethane, XYZCH, where X, Y, and Z are either H, Cl, or F, we estimated the vibrational frequencies in the activated complex by using those in the molecule XYZCF as guides, on the assumption that the C·H·OH portion of the activated complex is similar to the C-F portion of the real molecule. The vibrational-frequency changes in the activated complexes for all the halomethanes are summarized in Table 1. A more complete discussion of how these changes were derived is presented elsewhere 5.

For the haloethanes, it was not possible to examine each reaction in detail because there are more frequencies, fewer mode identifications, and fewer molecules for which detailed spectra are available. Instead, we compared the vibrational frequencies of CH_3CH_3, CH_3CH_2F, CH_3CHF_2, and CH_3CF_3, the change in the first pair representing the reaction of OH with all haloethanes with only β-H atoms (i.e., no H atoms on the same C atom as F or Cl atoms), and the changes between the second and third pairs representing reactions with α-H atoms. Because the experimental data[6] indicate that a reaction with haloethanes containing only β-H atoms is at least an order of magnitude slower than for haloethanes with some α-H atoms, we assumed that in those reagents containing both α- and β-H atoms the reaction with the β-H atoms can be neglected. The assumed changes are summarized in Table 2. In both kinds of reactions, we assume the newly formed C·H·O and H·O-H bonds have the same values that were used in the halomethane reactions (1000 cm^{-1} each).

TABLE 1. ASSUMED VIBRATIONAL-FREQUENCY CHANGES IN (OH + HALOMETHANE) REACTIONS

Reagent	Vibrational frequencies removed from reagent (cm^{-1})	Vibrational frequencies added in activated complex (cm^{-1})
CH_4	3100, 1300 (2)*	2100, 1000 (4)
CH_3Cl	3000, 1450, 1020 (2)	2100, 1250, 1000 (2), 750, 280
CH_2Cl_2	3000, 1470, 1150, 900, 280	2100, 1300, 1000 (2), 280 (2), 270
$CHCl_3$	3000, 1220 (2), 260(2)	2100, 1000 (2), 280 (3), 240 (2)
CH_3F	3000, 1470, 1180 (2)	2100, 1250, 1000 (2), 750, 400
CH_2F_2	3000, 1500, 1260, 1180	2100, 1370, 1000 (2), 400 (2)
CHF_3	3000, 1370 (2), 510 (2)	2100, 1000 (2), 400 (4)
CH_2FCl	3000, 1250, 1000	2100, 1000 (2), 400, 280
$CHCl_2F$	3000, 1300, 1240, 370	2100, 1000 (2), 400, 280 (2)
$CHClF_2$	3000, 1350, 1310, 600, 410 (2)	2100, 1000 (2), 500, 400 (2), 325 (2)
CH_3Br	3000, 1440, 950	2100, 1225, 1000 (2), 250

*Numbers in parentheses indicate number of vibrations.

TABLE 2. ASSUMED VIBRATIONAL-FREQUENCY CHANGES IN ACTIVATED COMPLEXES FOR (OH + HALOETHANE) REACTIONS

		Contribution to $\Delta S^{\ddagger}(300)$ (eu)
β-hydrogen abstraction (from CH_3 group)		
Frequencies removed from reagent		
C-H Stretch	(3000 cm^{-1})	0
CH_3 Rock	(800 cm^{-1})	-0.2
Frequencies added		
C·H Asym. Stretch	(Reaction coord.)	--
C·H Sym. Stretch	(2200 cm^{-1})	0
CC·H Bend	(240 cm^{-1})	1.8
C·H·O Bend	(1000 cm^{-1})	0.1
H·O-H Bend	(1000 cm^{-1})	0.1
α-hydrogen abstraction (from CH_2X or CHX_2 group)		
Frequencies removed from reagent		
C-H Stretch	(3000 cm^{-1})	0
CH_2 Def. or CCH Bend	(1400 cm^{-1})	0
CH_2 Def. or CCH Bend	(1300 cm^{-1})	0
Frequencies added to complex		
C·H Asym. Stretch	(Reaction Coord.)	--
C·H Sym. Stretch	(2200 cm^{-1})	0
CC·H Bends	(340 cm^{-1}; 2*)	2.4
C·H·O Bend	(1000 cm^{-1})	0.1
H·O-H Bend	(1000 cm^{-1})	0.1

*Number of bends.

Internal Rotations

The properties of the internal rotations must be evaluated accurately because considerable entropy is associated with these two degrees of freedom. The moments of inertia for the internal rotations are calculated by the procedure of Herschbach et al.[7] The entropy of free rotation is given by $S_f = R(\ln Q + 1/2)$, where $Q = 0.35(I_r T)^{1/2}/\sigma$ for I_r, the reduced moment of inertia, in dalton-Å. Here σ is the symmetry of the internal rotation, which is 1 for most of the reagents considered in this report but 3 for rotation about the C-H bond in CH_4, $CHCl_3$, and CHF_3. For rotation about the C-H bond, $Q \approx 6.2/\sigma$ for all halomethanes and 1.8 for CH_4. For rotation about the O-H bond, $Q \approx 5.9$ for all halomethanes and 5.1 for CH_4. The corrections to the entropy due to the barrier to rotation, $S_f - S_h$, are interpolated from tables developed by Pitzer and coworkers,[8] where S_h = entropy of hindered rotation.

For all the haloethanes, the reduced moment of inertia I_r for rotation about the C·H bond is approximately 1.1 in dalton-Å, which makes the partition function Q equal to 6.5, and the entropy of free rotation S_f, 4.7 eu. For rotation about the H·O bond, $I_r = 0.95$, $Q = 6.0$, and $S_f = 4.6$ eu.

Unlike the halomethanes, the haloethanes already have one internal rotation--about the C-C bond. In a previous study involving transition-state theory calculations for reactions of O atoms with alkanes,[3] we obtained reasonable agreement with the experimental value by assuming that the barrier to internal rotation was lowered by 1 kcal/mol in the activated complex. The same assumption was made here. The contributions to $\Delta S^{\ddagger}$ are shown in Table 4 (p. 16). There is a qualitative difference between the reactions abstracting α-H atoms and those abstracting β-H atoms, because the OH adduct makes a much greater change in the moment of inertia of a CH_3 group than it does when added to a halomethyl group. Further details are published elsewhere 5.

EMPIRICAL CORRELATIONS

After carrying out the detailed transition-state theory calculations outlined above, we applied the results of those calculations to establish simple empirical correlations between activation entropy and activation energy for an arbitrary (OH + haloalkane) reaction with readily determined molecular

parameters. The following procedure generates simple, approximate expressions for $\Delta S^{\ddagger}(298)$ and for $E(298)$ without requiring more information than the molecular weight of the reacting haloalkane and its gross structural details.

Entropy of Activation

In Ref. 5 we showed that the entropy of the activated complex, $S^{\ddagger}$, was calculated from the entropy of the reacting haloalkane RH by a series of corrections terms:

$$S^{\ddagger} = S^{0}_{RH} + \Delta S_t + \Delta S_v + \Delta S_r + \Delta S_{ir} + \Delta S_e + \Delta S_\sigma + \Delta S_n \qquad (5)$$

where the ΔS terms represent the corrections required in replacing the properties (translation, vibration, rotation, internal rotation, electronic, symmetry, optical isomerism, respectively) of the haloalkane by those of the activated complex. The translational contribution ΔS_t is given by $(3/2)R \ln(M^{\ddagger}/M)$; therefore, it will decrease to zero as the mass M of the reagent RH increases (since $M^{\ddagger} = M + M_{OH}$). The rotational contribution ΔS_r is given by $(1/2)R \ln[(I_a I_b I_c)^{\ddagger}/(I_a I_b I_c)]$, where the three I factors are the principal moments of inertia. Each I depends approximately on M; hence, ΔS_r too will decrease to zero as the size of the reagent haloalkane (and hence its molecular weight) increases. The vibrational contribution ΔS_v is the sum of contributions from the vibrational modes, each of which varies approximately with vibrational frequency. In our procedure, several vibrational modes, all of comparable frequencies in different reagents, are replaced by other modes in the activated complexes, modes for which the frequencies are comparable for different reactions. A similar argument, though somewhat weaker, can be made for internal rotations. Tables 3 and 4 show that the contributions from both vibrations and internal rotations are approximately constant. The remaining three terms on the right-hand side of Eq. (5) are independent of mass. These arguments suggest that there might be some correlation between $\Delta S^{\ddagger}(298)$ and M, a suggestion that is borne out by examining the second and last columns of Tables 3 and 4. The results of this approach are given in Section 5.

TABLE 3. CALCULATED CONTRIBUTIONS TO $\Delta S^{\ddagger}(298)$ FOR (OH + HALOMETHANE) REACTIONS*

Reagent	MW†	ΔS_t	ΔS_r	ΔS_e	ΔS_σ	ΔS_n	σ_{int}	Internal rotation (C·H) Q_f	Internal rotation (C·H) S_f	Internal rotation (H·O) Q_f	Internal rotation (H·O) S_f	$(\Delta S_{ir})^{\ddagger}$	$(\Delta S_v)^{\S}$	$\Sigma\Delta S$	$(S^{\ddagger})^{\|}$	$(S^{\ddagger})^{\#}$	$(S^{\ddagger}_{exp})^{**}$
CH_3Cl	50	0.9	4.8	1.4	2.2	0	1	5.9	4.5	6.2	4.3	8.8	1.8	19.9	75.9	-24.0	-27.3
CH_2Cl_2	85	0.5	3.0	1.4	1.4	0	1	5.9	4.5	6.2	4.3	8.8	3.2	18.3	82.9	-25.6	-26.0
$CHCl_3$	119	0.4	1.0	1.4	2.2	0	3	2.0	2.4	6.2	4.3	6.7	3.5	15.2	85.8	-28.7	-26.2
CH_3F	34	1.2	5.0	1.4	2.2	0	1	5.9	4.5	6.2	4.3	8.8	1.3	19.9	73.1	-24.0	-26.5
CH_2F_2	52	0.8	3.7	1.4	1.4	0	1	5.9	4.5	6.2	4.3	8.8	2.1	18.2	77.1	-25.7	-26.9
CHF_3	70	0.6	2.6	1.4	2.2	0	3	2.0	2.4	6.2	4.3	6.7	2.7	16.2	78.2	-27.7	-28.0
CH_2ClF	68	0.7	3.3	1.4	0	1.4	1	5.9	4.5	6.2	4.3	8.8	2.6	18.2	81.4	-25.7	-27.8
$CHCl_2F$	103	0.5	2.0	1.4	0	0	1	5.9	4.5	6.2	4.3	8.8	3.2	15.8	85.8	-28.1	-29.0
$CHClF_2$	86	0.5	2.2	1.4	0	0	1	5.9	4.5	6.2	4.3	8.8	3.0	15.9	83.0	-28.0	-30.6
CH_3Br	95	0.5	4.9	1.4	2.2	0	1	5.9	4.5	6.2	4.3	8.8	1.8	19.6	78.4	-24.3	-29.1

*All entropies in eu (cal mol^{-1} K^{-1}), and at 298 K.

†Molecular weight, daltons.

‡ΔS_{ir} sum of S_f for two internal rotations.

§ΔS_v based on assumed vibrations of Table 2.

|$S^{\ddagger} = \Sigma\Delta S + S^0_{RH}$.

#$\Delta S^{\ddagger} = S^{\ddagger} - S^0_{RH} - S^0_{OH}$.

**From Refs. 1 and 9.

TABLE 4. CALCULATED CONTRIBUTIONS TO $\Delta S^{\ddagger}$ FOR REACTIONS OF OH WITH HALOETHANES

Reagent	M	ΔS_t	ΔS_r	ΔS_e	$\Delta S_{\sigma+n}$	ΔS_v	ΔS_{ir}	$\Sigma\Delta S$	$\Delta S^{\ddagger}$	$\Delta S^{\ddagger}$/H atom
$CH_3\underline{CH_2}Cl$*	64	0.7	2.2	1.4	1.4	2.6	9.7	18.0	-25.8	-27.2
$CH_3\underline{CH_2}F$	48	0.9	3.0	1.4	1.4	2.6	9.8	19.1	-24.8	-26.2
CH_3CHCl_2	98	0.5	1.8	1.4	0	2.6	9.7	16.0	-27.8	-27.8
CH_3CHF_2	66	0.7	2.2	1.4	0	2.6	9.6	16.5	-27.4	-27.4
CH_2FCH_2F	66	0.7	2.2	1.4	2.8	2.6	10.0	19.7	-24.2	-27.0
CH_2BrCH_2Br	188	0.3	0.5	1.4	2.8	2.6	9.5	17.1	-26.8	-29.6
$\underline{CH_2}ClCHCl_2$	132	0.4	0.8	1.4	1.4	2.6	9.7	16.3	-27.6	
$CH_2ClC\underline{H}Cl_2$	132	0.4	0.5	1.4	0	2.6	9.5	14.4	-29.5	
$\langle CH_2ClCHCl_2\rangle$†	132	0.4	0.65	1.4	2.2	2.6	9.6	16.9	-27.0	$\langle$-29.2$\rangle$
$\underline{CH_2}FCHF_2$	84	0.6	1.7	1.4	1.4	2.6	9.9	17.6	-26.3	
$CH_2FC\underline{H}F_2$	84	0.6	1.6	1.4	0	2.6	9.6	15.8	-28.1	
$\langle CH_2FCHF_2\rangle$†	84	0.6	1.7	1.4	2.2	2.6	9.8	18.3	-25.6	$\langle$-27.8$\rangle$
CH_2ClCF_2Cl	134	0.4	1.2	1.4	1.4	2.6	9.7	16.7	-27.2	-28.6
CH_2ClCF_3	118	0.4	1.2	1.4	1.4	2.6	9.9	16.9	-27.0	-28.4
CH_2FCF_3	102	0.5	1.7	1.4		2.6	9.9	17.5	-26.4	-27.8
CHF_2CHF_2	102	0.5	1.2	1.4	1.4	2.6	9.9	17.0	-26.9	-28.3
$CHCl_2CF_3$	152	0.3	0.5	1.4	0	2.6	9.5	14.3	-29.6	-29.6
$CHClFCF_3$	136	0.3	0.7	1.4	0	2.6	9.6	14.6	-29.3	-29.3
CHF_2CF_3	120	0.4	0.9	1.4	0	2.6	10.0	15.3	-28.6	-28.6
CH_3CCl_3	132	0.4	1.4	1.4	2.2	2.0	11.7	19.1	-24.8	-27.0
CH_3CF_3	138	0.4	2.2	1.4	2.2	2.0	12.1	20.3	-23.6	-25.8
CH_3CF_2Cl	100	0.5	1.9	1.4	0	2.0	13.8	19.6	-24.3	-26.5

*For reagents with two different kinds of H atoms, the one being abstracted is underlined.

†Average of two different reaction paths.

Activation Energy

Previously, workers attempted to correlate activation energies with bond dissociation energies (BDEs) of the dissociating bond. This approach was tried with moderate success for (OH + halomethane) reactions; results are plotted in Fig. 1. However, the same could not be done profitably for the haloethanes because BDEs are known for very few of the compounds. Instead, we attempted to make an empirical correlation of the activation energies with a set of six structural parameters. Each parameter describes the correction to the activation energy of CH_4 that must be made as H atoms are substituted by F, Cl, CH_3, CH_2X, CHX_2, or CX_3, where X = F or Cl. (At present there are temperature-dependent rate data for only one brominated haloalkane, so we have confined our attention to fluorinated and chlorinated compounds until more data become available.) In other words,

$$E(298)/R = E(CH_4)/R - a_F n_F - a_{Cl} n_{Cl} - a_{CH_3} n_{CH_3} - a_{CH_2X} n_{CH_2X} - a_{CHX_2} n_{CHX_2} - a_{CX_3} n_{CX_3} \quad (6)$$

The calculated activation energies for all halomethanes and haloethanes (except CHF_3 and CH_3CF_3, which pose unique problems), which were derived from the experimental values of k(298), were used in deriving the values of the various a_i. The results of this effort are given in Section 5.

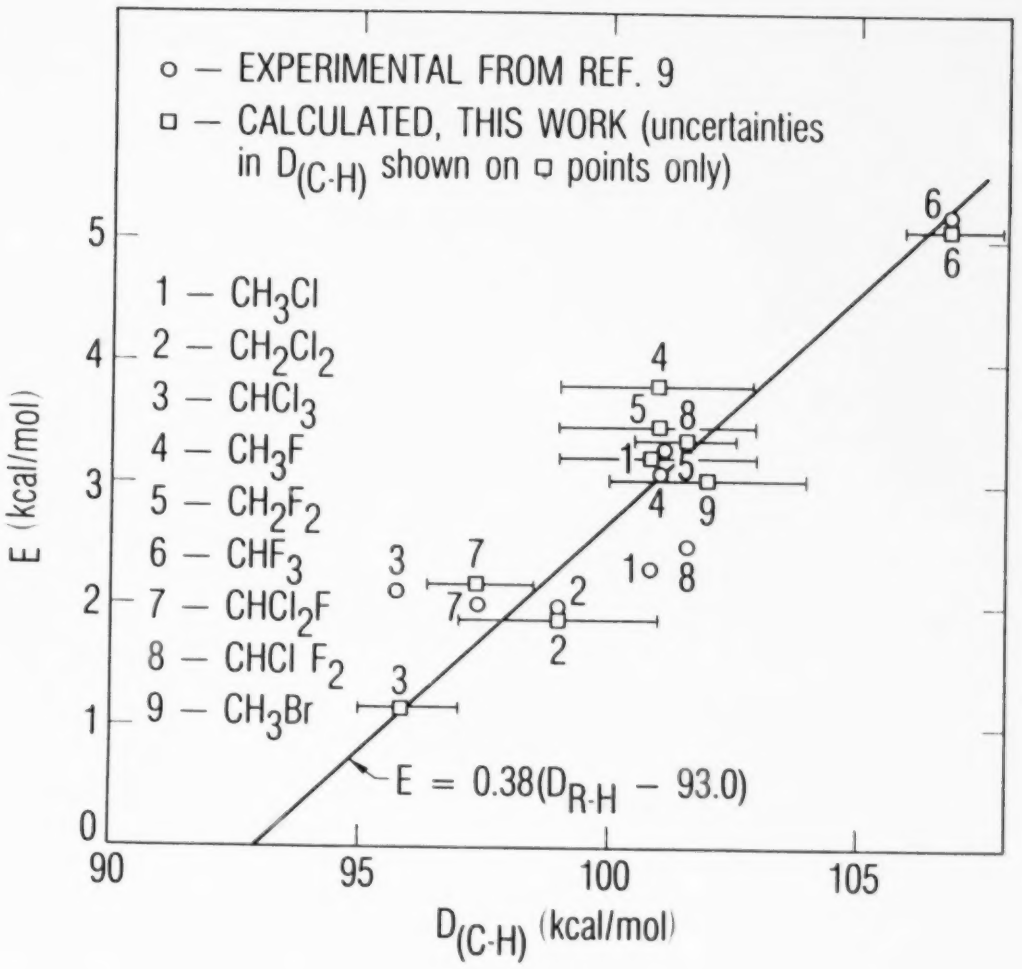


Figure 1. Correlation of activation energy E(298) for (OH + halomethane) reactions with bond dissociation energy D_{RH} of halomethane.

SECTION 5

RESULTS AND DISCUSSION

TRANSITION-STATE THEORY CALCULATIONS

OH + Haloalkanes

Transition-state theory calculations were carried out using the vibrational-frequency changes of Tables 1 and 2, the entropies of activation listed in the last columns of Tables 3 and 4, and the experimental values of k(298) listed in the second column of Tables 5 and 6. Selected results are shown in Figs. 2 through 11, together with the experimental data; these include examples showing typical agreement as well as best- and worst-case fits. Plots for other reactions are given elsewhere 5. In addition, calculated three-parameter Arrhenius expressions for all 28 haloalkanes are listed in Tables 5 and 6. Those tables show that the temperature exponents n for all the α-H abstractions are 1.6 to 1.7, whereas for the three β-H abstraction reactions n = 1.1.

For the halomethanes, two models were used for each reaction: one with hindered internal rotation and one with free internal rotation. The two models were otherwise identical. On the average, the free internal rotation model appears to give slightly better agreement with the data. In Fig. 2 we show the calculated rate coefficients for both the free and hindered rotation cases; in the other figures only the free internal rotation model results are plotted. The difference between the free and hindered rotation calculations is comparable to that shown in Fig. 2. For the haloethanes, only the free internal rotation model was used, and the value for all but one agreed with experimental data to within the experimental uncertainties. The discrepancies between experimental and calculated rate coefficients were no greater than 25%.

The single puzzling exception is $CHCl_3$, for which both models greatly underpredict the activation energy and hence the rate coefficients at T > 300 K. To obtain agreement with the data requires a greatly increased $\Delta S^{\ddagger}(298)$--from -28.7 to ~-25.3 eu--for the free internal rotation case. One

TABLE 5. CALCULATED RATE COEFFICIENTS FOR (OH + HALOMETHANES)*

Reagent	Experimental log k(298)†	Calculated Rate Coefficient, $k = AT^n \exp(-B/T)$ log A‡	n	B	E(298)/R**
CH_4	6.71	5.71	1.4	1710	2160
CH_3Cl	7.40	5.70	1.4	1230	1660
CH_2Cl_2	8.00	4.78	1.6	520	1010
$CHCl_3$	7.80	3.82	1.7	170	680
CH_3F	7.00	5.41	1.5	1480	1940
CH_2F_2	6.81	4.45	1.7	1290	1820
CHF_3	5.10	3.76	1.8	2160	2690
CH_2ClF	7.46	4.75	1.6	870	1370
$CHCl_2F$	7.30	3.96	1.7	610	1110
$CHClF_2$	6.45	3.69	1.8	1180	1720
CH_3Br	7.40	5.92	1.3	1200	1620

*CH_4 from Ref. 5; values for halomethanes calculated for model assuming free internal rotation in activated complex. For model with hindered internal rotation (see text for details), multiply the expressions for k in the table by $0.08\ T^{0.3} \exp(250/T)$. E(298)/R is then smaller by 180.

†All values from Ref. 1 except for CH_3Br, which is from Ref. 9.

‡AT^n in L mol^{-1} s^{-1}; B in kelvins.

**$E(298)/R = -d(\ln k)/d(1/T)$ at 298 K.

TABLE 6. CALCULATED RATE COEFFICIENTS FOR (OH + HALOETHANES)

Reagent	Experimental log k(298)	Ref.	Calculated $k(T) = AT^n \exp(-B/T)$ Log A	n	B	E(298)/R*
CH_3CH_2Cl	8.37	13,14	4.76	1.6	250	730
CH_3CH_2F	8.14	16	4.97	1.6	550	1030
CH_3CHCl_2	8.20	13	4.32	1.6	60	530
CH_3CHF_2	7.48	13,15,16,20	4.40	1.6	610	1100
CH_2FCH_2F	7.83	21	4.79	1.7	810	1320
CH_2BrCH_2Br	8.20	13	4.25	1.7	180	690
$CH_2ClCHCl_2$	8.28	17,19	4.20	1.7	100	590
CH_2FCHF_2	7.47	20,21	4.49	1.7	860	1390
CH_2ClCF_2Cl	7.20	17,18	4.18	1.7	810	1310
CH_2ClCF_3	6.95	13,15,20	4.20	1.7	1020	1520
CH_2FCF_3	6.70	17,20,21	4.32	1.7	1270	1780
CHF_2CHF_2	6.50	20	4.20	1.7	1330	1840
$CHCl_2CF_3$	7.40	13,18,20	3.64	1.7	310	810
$CHClFCF_3$	6.87	13,18	3.70	1.7	720	1230
CHF_2CF_3	6.48	20,21	4.15	1.6	1130	1600
CH_3CCl_3	6.80	13,17,19,20,22-24	6.38	1.1	1610	1960
CH_3CF_3	5.95	20,21	6.61	1.1	2350	2730
CH_3CF_2Cl	6.60	13-15,20,23	6.48	1.1	1800	2180

*$E(298)/R = -d(\ln k)/d(1/T)$ at 298 K.

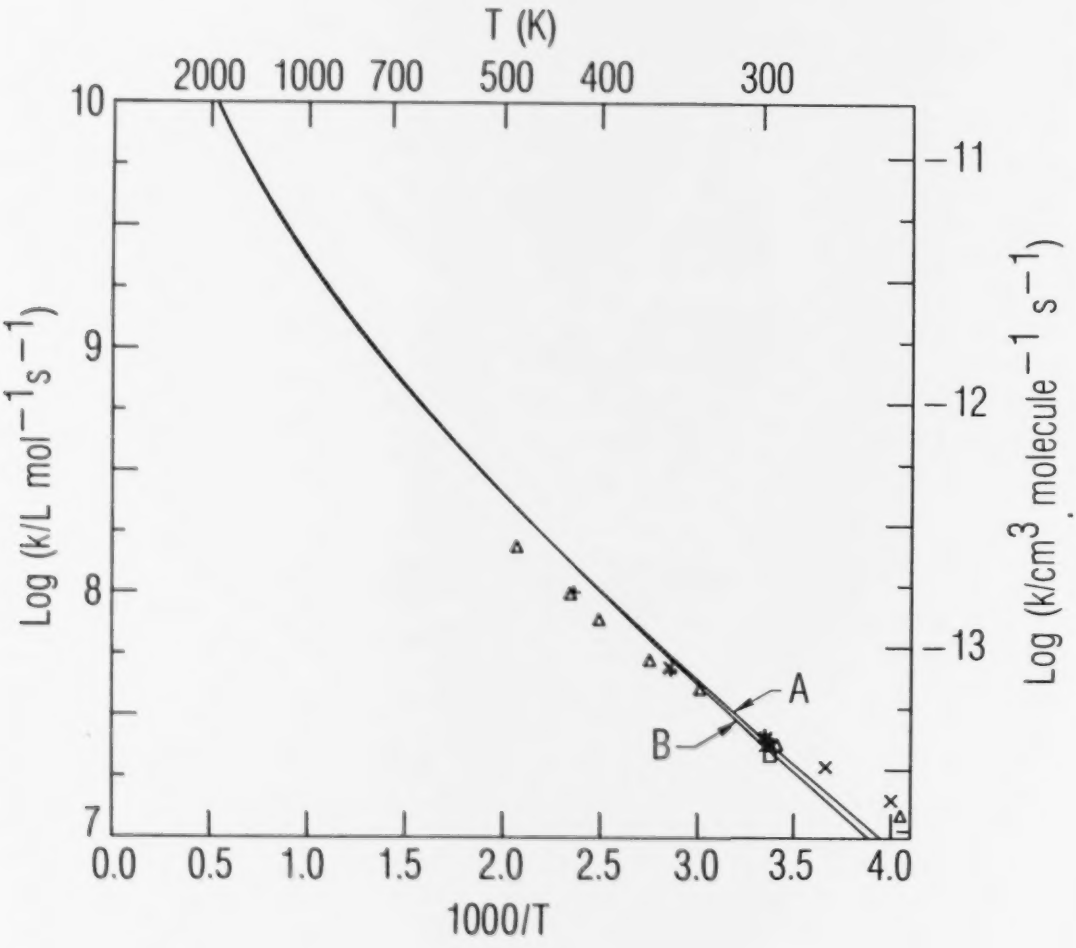


Figure 2. Rate coefficients for (OH + CH_3Cl) reaction. Curve A from transition-state theory calculations of Ref. 2. Curve B calculated from Eq. (4). Δ: Ref. 9; ×: Ref. 10; □: Ref. 11; +: Ref. 12; ∇: Ref. 13.

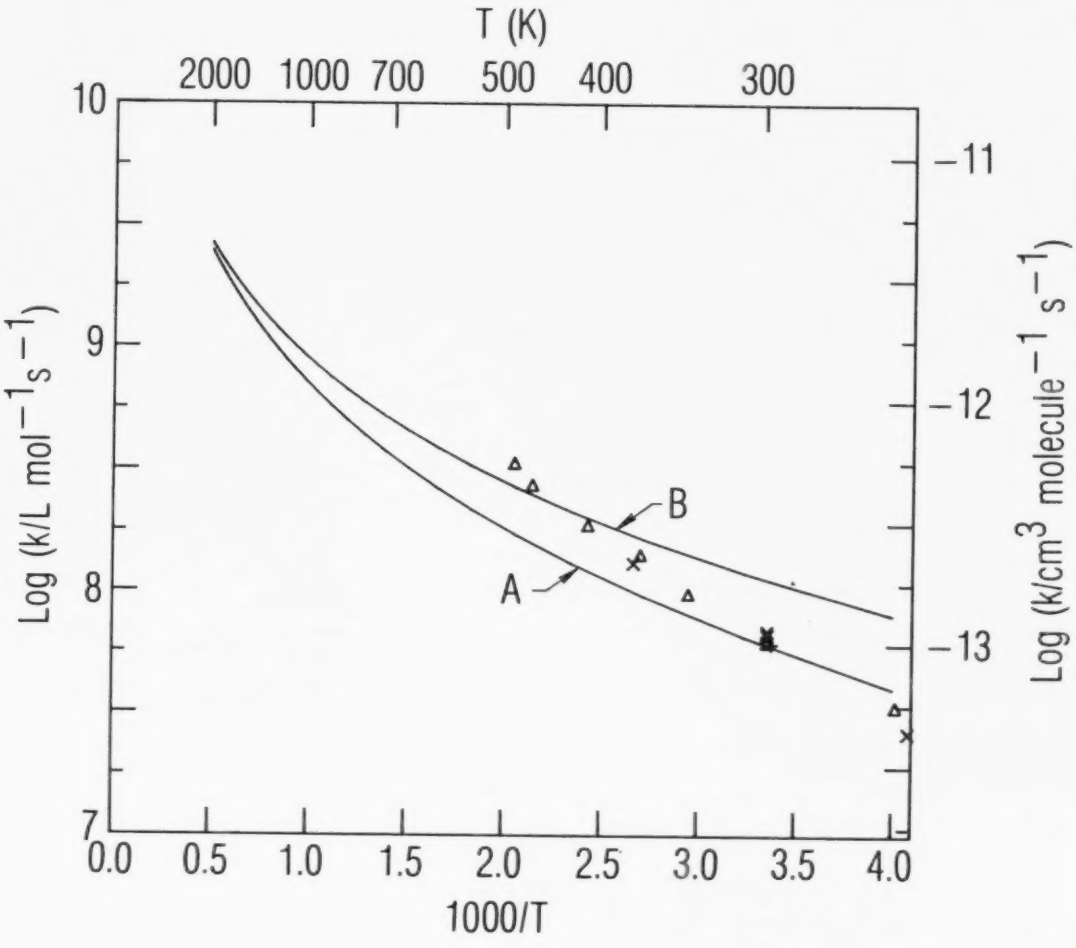


Figure 3. Rate coefficients for (OH + $CHCl_3$) reaction. Δ: Ref. 9; ×: Ref. 10; +: Ref. 11. Curves A and B calculated same as those in Fig. 2.

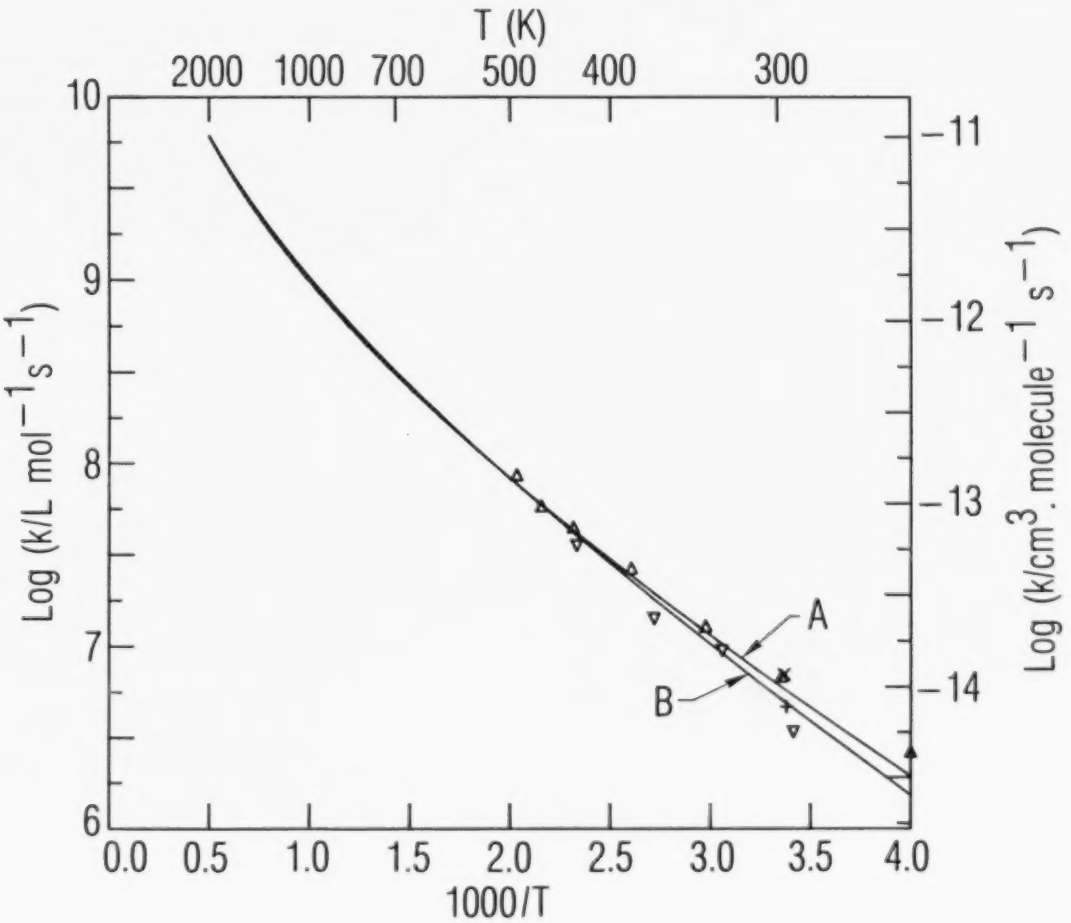


Figure 4. Rate coefficients for (OH + CH_2F_2) reaction. Δ: Ref. 9; +: Ref. 11; ×: Ref. 14; ∇: Ref. 15. Curves A and B calculated same as those in Fig. 2.

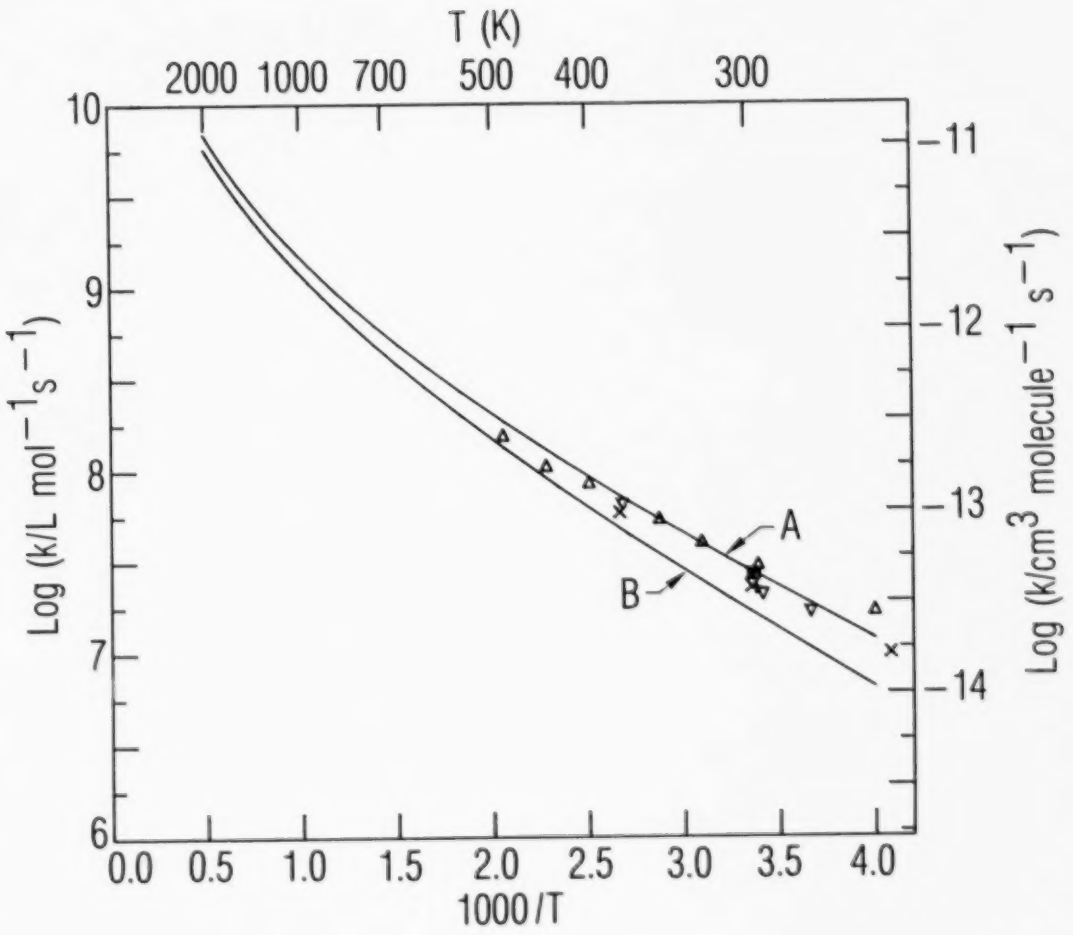


Figure 5. Rate coefficients for (OH + CH_2ClF) reaction. Δ: Ref. 9; ×: Ref. 10; +: Ref. 11; □: Ref. 13; ▽: Ref. 16. Curves A and B calculated same as those in Fig. 2.

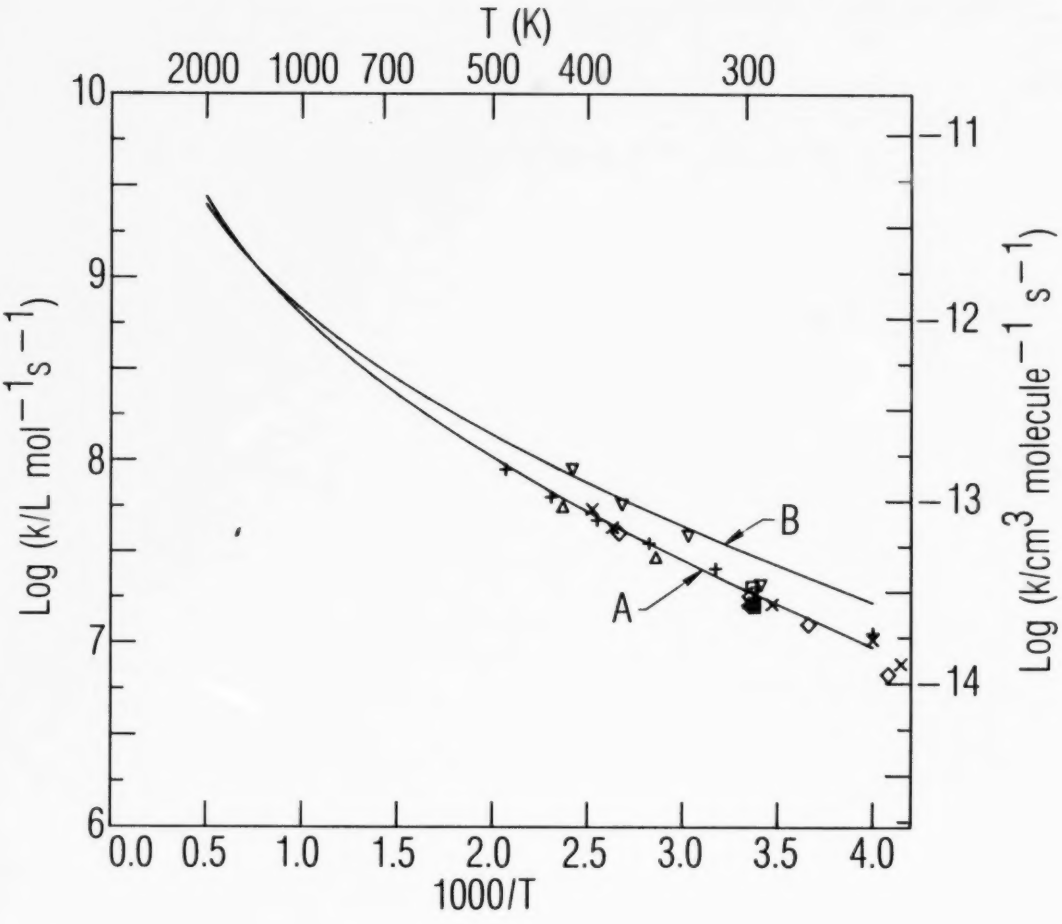


Figure 6. Rate coefficients for (OH + $CHCl_2F$) reaction. +: Ref. 9; ■: Ref. 11; Δ: Ref. 12; □: Ref. 13; ∇: Ref. 15; ×: Ref. 17; ◇: Ref. 18. Curves A and B calculated same as those in Fig. 2.

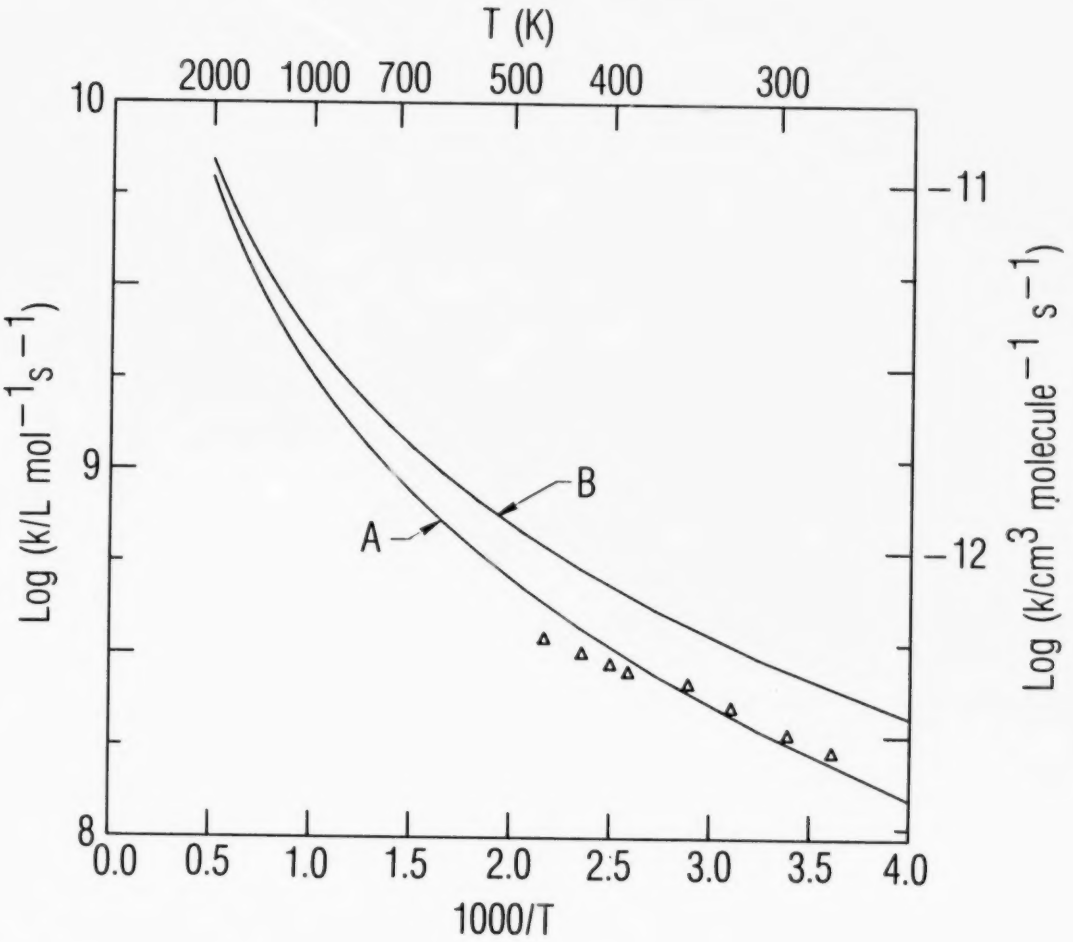


Figure 7. Rate coefficients for (OH + $CH_2ClCHCl_2$) reaction. Δ: Ref. 19. Curves A and B calculated same as those in Fig. 2.

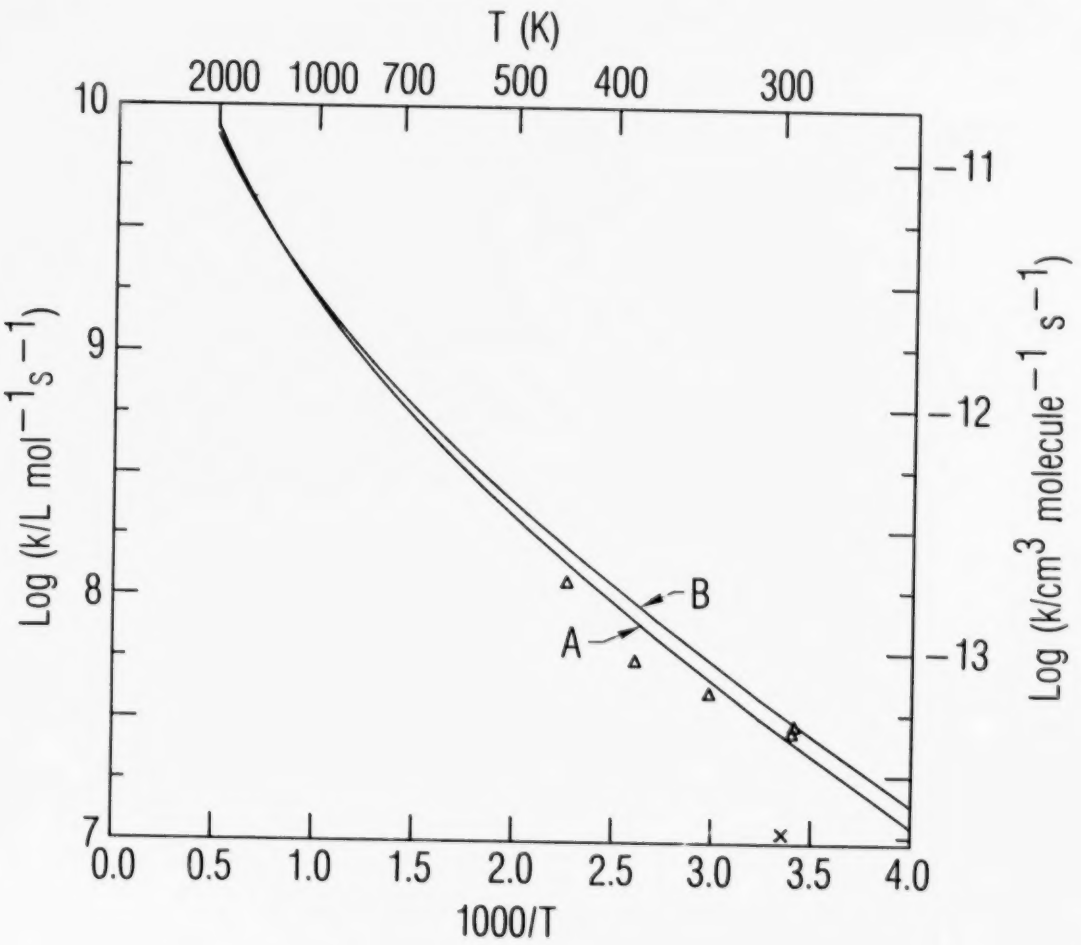


Figure 8. Rate coefficients for (OH + CH_2FCHF_2) reaction. Δ: Ref. 15; ×: Ref. 19. Curves A and B calculated same as those in Fig. 2.

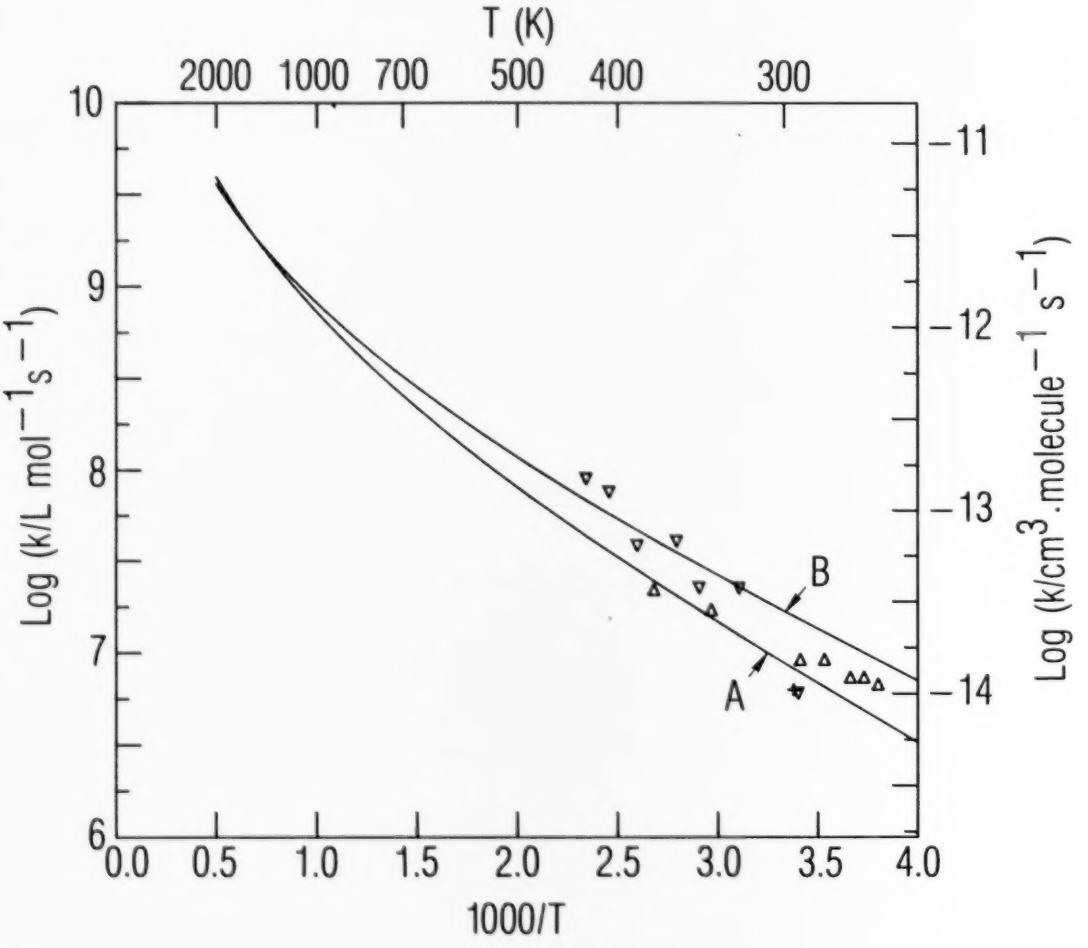


Figure 9. Rate coefficients for (OH + CH_2ClCF_3) reaction. ∇: Ref. 15; Δ: Ref. 16; +: Ref. 20. Curves A and B calculated same as those in Fig. 2.

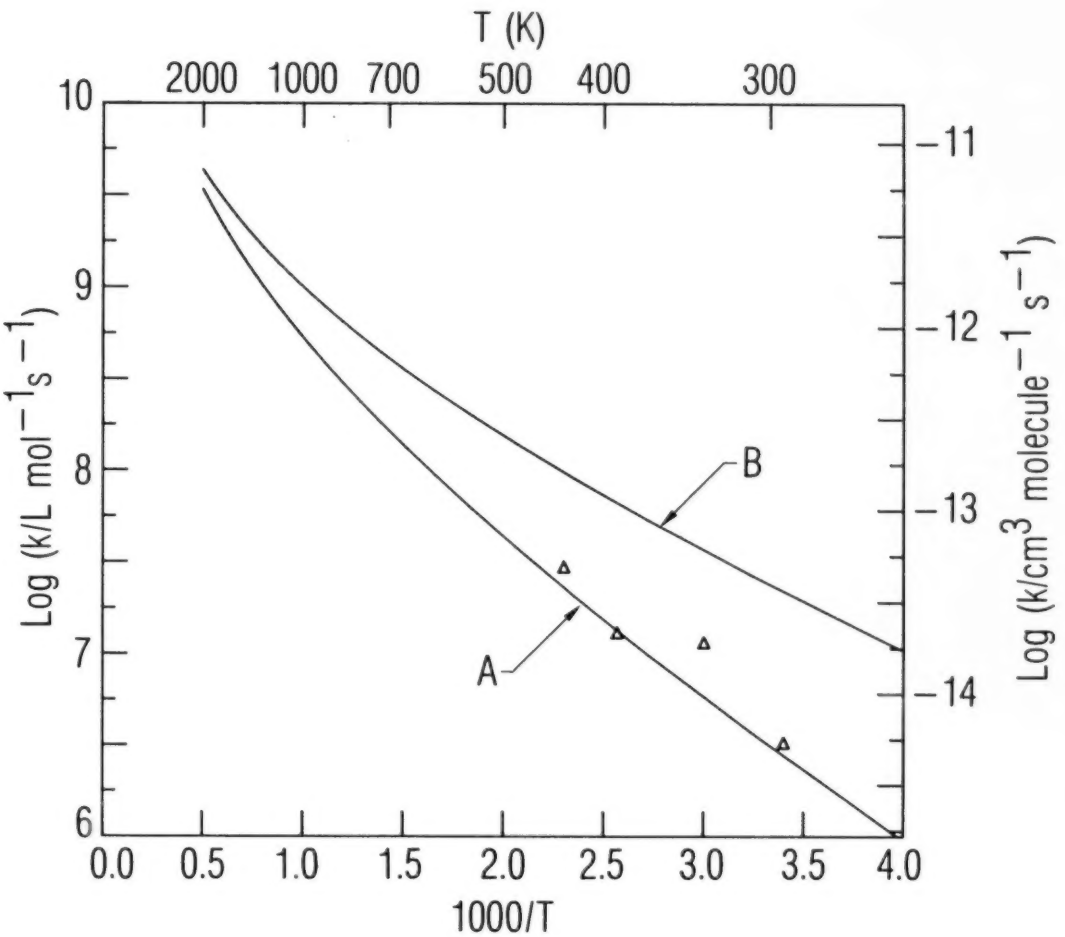


Figure 10. Rate coefficients for (OH + CHF_2CHF_2) reaction. Δ: Ref. 15. Curves A and B calculated same as those in Fig. 2.

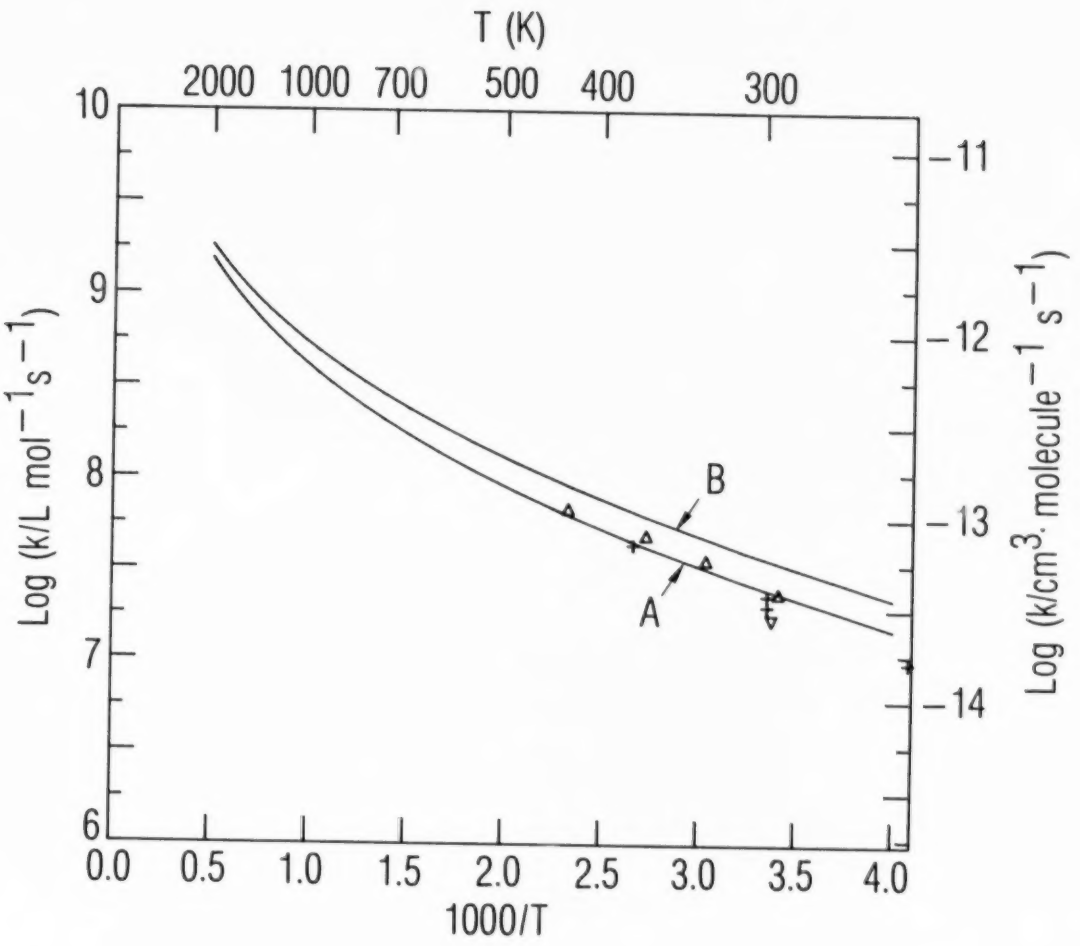


Figure 11. Rate coefficients for (OH + $CHCl_2CF_3$) reaction. Δ: Ref. 15; ∇: Ref. 20; +: Ref. 21. Curves A and B calculated same as those in Fig. 2.

way agreement is achieved is by lowering the four low-frequency vibrations in the activated complex to 150 cm^{-1}. However, there is no a priori reason for making the frequencies of this one complex so much lower than those of all the others.

The discrepancy between the calculated and experimental values of k(T) for this halomethane suggests either that k(300) is really larger than the measured value or, more likely, that at higher temperatures (400-500 K) another process removing OH radicals is occurring. The likelihood of experimental errors near 300 K seems slight, given the close agreement among the three independent measurements of k(300).[1,9,10] The possibility of impurities contributing to k(T) at higher temperatures seems unlikely because Jeong and Kaufman[1] were careful to ensure the impurity level of their reagent to be less than 10 ppm. Even an impurity that reacted with OH at every collision would have to be present in the parts-per-thousand range to account for so large a contribution to k(500).

Because of the possible serious consequences for the applications of the thermochemical approach to conventional transition-state theory as we have been using it, we recommend that the (OH + $CHCl_3$) reaction rate be carefully remeasured over a temperature range sufficiently wide to eliminate any doubts concerning both the absolute value of the rate coefficients and the activation energy.

Comparison with Previous Calculations

Jeong and Kaufman[1] carried out similar transition-state theory calculations for the nine (OH + haloalkane) reactions they studied experimentally. They concluded that their theoretical A factors were in good agreement with the experimental ones (all at 298 K) on the average, but with inexplicably large deviations in both directions for individual reactions--more than a factor of 2 in four cases.

Most of our calculated values for $S^{\ddagger}(298)$ [and hence, for A(298)] are in good agreement with the calculations of Jeong and Kaufman: within 1 eu (for the free internal rotation models) for all but two reagents (CH_2F_2, CH_2ClF), and those within 2 eu. (A difference in 1 eu in $\Delta S^{\ddagger}$ means a difference of a

factor of 1.65 in the A factor.) The discrepancies are due mainly to different assignments of vibrational frequencies and different treatment of internal rotations. Nevertheless, as Figs. 2 and 4 through 11 demonstrate, our calculated values of k(T) are in good agreement with the experimental data--much better than the discrepancies in A(298) would suggest. This demonstrates not that our calculations are better than theirs, but that using k(298) has advantages for calculating k(T) at higher temperatures: Over the relatively narrow temperature range of the experiments, the errors in A(298) and E(298) compensate each other. For example, an error in the calculated value of $\Delta S^{\ddagger}(298)$ of 1 eu will propagate an error in the calculated values of log k(600) and log k(1000) of 0.11 and 0.15 log units, respectively. An error of 2 eu yields errors of 0.22 and 0.31, respectively. Errors less than 0.2 log units are generally very difficult to detect.

Accuracy of Arrhenius and Modified Arrhenius Parameters

It is useful to turn the latter argument around and consider the limits on accuracy of Arrhenius parameters derived from experimental data over limited temperature ranges. If data are taken at 300 and 600 K, 10% errors in k(300) and k(600) of opposite sign will propagate an error in the activation energy [for k expressed as A exp(-E/RT)] of 240 cal/mol. Errors of 20% in opposite directions yield an error of 440 cal/mol.

The difficulties in extracting parameters for the modified Arrhenius expression, $k = AT^n \exp(-B/T)$, are even greater. Suppose k(T) is measured over an interval of T_1 to T_2. If a three-parameter expression is derived that yields $k(T_m)$ and also $d[\ln k(T_m)]/d(1/T)$ correctly at some midpoint (T_m) temperature, an error of 0.5 in n propagates only a 15% error in $k(T = 2T_m)$ and a 20% error in $k(T = 3T_m)$. In other words, unless k(T) is measured with great precision over a very large temperature range, it will be more accurate to estimate the value of n from a theoretical calculation than to extract it from experimental data.

EMPIRICAL CORRELATIONS

Activation Entropies

In Fig. 12, $\Delta S^{\ddagger}(298)$ is plotted for the free internal rotation model versus the molecular weight M of the reacting haloalkane for all the α-hydrogen abstractions. The least-squares fit through all the points is described by

$$\Delta S^{\ddagger}(298)\ (\text{eu/H atom}) = -2.2 \ln M - 18.0 \qquad (7)$$

or

$$\Delta S^{\ddagger}(298) = -2.2 \ln M - 18.0 + R \ln n_H$$

where S is in eu, M is in daltons, and n_H is the number of abstractable α-H atoms. This expression fits all the data with a maximum error of 1.4 eu and an average error of 0.3 eu. [The values of $\Delta S^{\ddagger}$ for CH_3CCl_3, CH_3CF_3, and CH_3CF_2Cl, which have only β-H atoms, are all 2 to 3 eu larger than Eq. (2) predicts.] When M becomes large enough (approximately 220 daltons), the contributions to ΔS_t and ΔS_r will be close to zero, and $\Delta S^{\ddagger}(298)$ per H atom should reach a minimum value of ~-30.3 eu.

Activation Energies

Using the approach outlined above, a least-squares fitting program was applied to activation energies for 28 (OH + haloalkane) reactions to solve for the parameters a_i of Eq. (6). The derived values, based on $E(CH_4)/R = 2100$ at 298 K, are:

$a_F = 85$	$a_{CH_2X} = 600$
$a_{Cl} = 515$	$a_{CHX_2} = 650$
$a_{CH_3} = 950$	$a_{CX_3} = 250$

The values of E(298)/R predicted with Eq.(6) are compared with the experimentally derived values in Table 7. The discrepancy between predicted and derived values is never worse than 570 (i.e., an error in E of 1.1 kcal/mol) and for most reagents is considerably smaller: The average error is 150 (i.e., 0.3 kcal/mol).

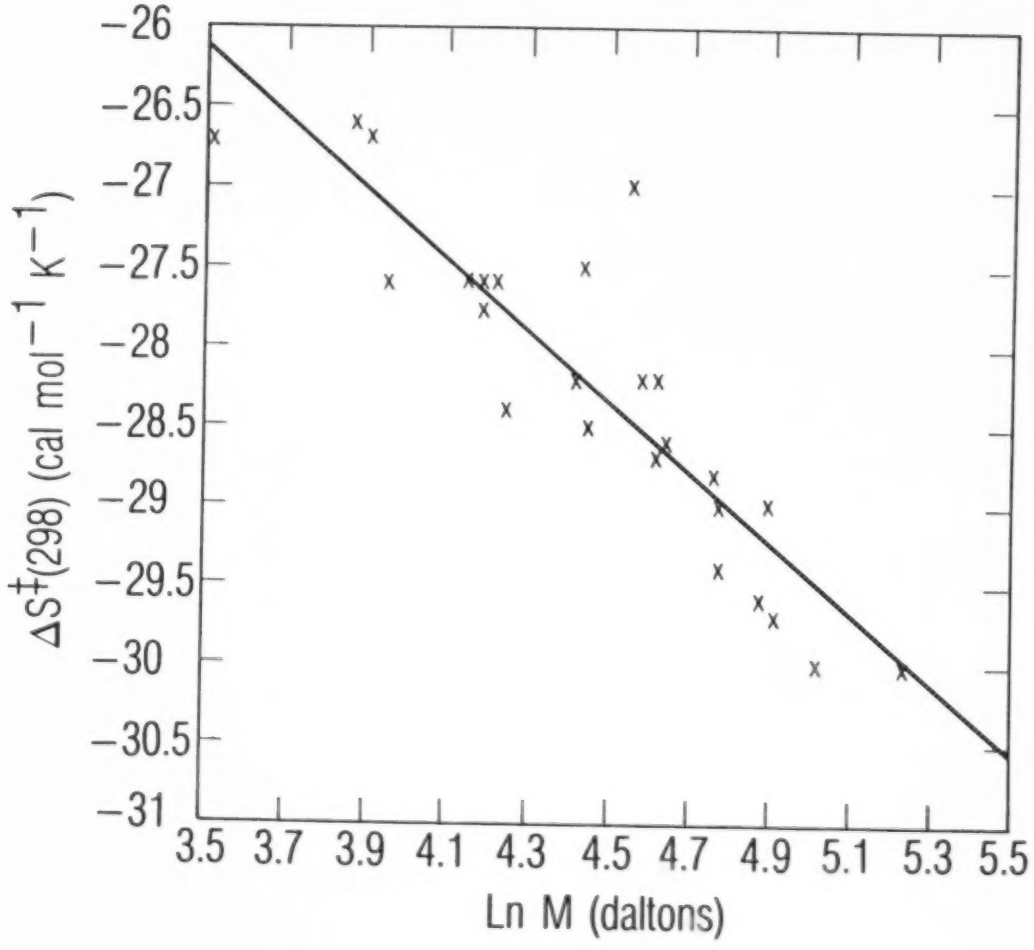


Figure 12. Correlation of activation entropy $\Delta S^{\ddagger}(298)$ per H atom (in eu) for (OH + haloalkanes), with ln M (in daltons) of haloalkane.

TABLE 7. ESTIMATED $\Delta S^{\ddagger}(298)$, E(298), AND k(298) FOR (OH + HALOALKANE) REACTIONS

Reagent	$\Delta S^{\ddagger}(298)^{*}$	$\Delta S^{\ddagger}(298)^{\dagger}$	$E(298)/R^{\ddagger}$	$E(298)/R^{\S}$	Log k(298)‖	Log k(298)#
CH_3Cl	-26.5	-26.2	1590	1620	7.40	7.36
CH_2Cl_2	-27.7	-27.0	1070	930	7.75	8.00
$CHCl_3$	-28.5	-28.7	560	580	8.05	7.80
CH_3F	-25.7	-26.2	2010	1900	6.95	6.95
CH_2F_2	-26.6	-27.1	1930	1730	6.71	6.81
CHF_3	-27.3	-27.7	--	2600	--	5.10
CH_2ClF	-27.2	-27.1	1500	1290	7.22	7.46
$CHCl_2F$	-28.2	-28.1	990	1040	7.49	7.30
$CHClF_2$	-27.8	-28.0	1420	1650	6.93	6.45
CH_3CH_2Cl**	-27.1	-27.4	630	730	8.51	8.37
CH_3CH_2F**	-26.5	-26.2	1060	1030	8.00	8.14
CH_3CHCl_2**	-28.1	-27.8	120	530	8.77	8.20
CH_3CHF_2**	-27.2	-27.4	980	1100	7.69	7.48
CH_2FCH_2F	-27.2	-27.0	960	1320	7.66	7.83
$CH_2ClCHCl_2$	-28.7	<-29.2>††	480,930	590	8.47‡‡	8.28
CH_2FCHF_2	-27.7	<-27.8>††	1330,1360	1390	7.52‡‡	7.47
CH_2ClCF_2Cl	-28.8	-28.6	1340	1310	7.15	7.20
CH_2ClCF_3	-28.5	-28.4	1335	1520	7.21	6.95
CH_2FCF_3	-28.2	-27.8	1760	1780	6.66	6.70
CHF_2CHF_2	-28.2	-28.3	1275	1840	7.36	6.50
$CHCl_2CF_3$	-29.1	-29.6	820	810	7.56	7.40
$CHClFCF_3$	-28.8	-29.3	1250	1230	6.98	6.87
CHF_2CF_3	-28.5	-28.6	1680	1600	6.41	6.48
CH_3CCl_3		-27.0	1850	1960	6.61	6.80
CH_3CF_2Cl		-26.5	1850	2180	6.73	6.60

*Calculated from Eq. (7); per H atom.

†Calculated; from Tables 3 and 4; per H atom.

‡Calculated; from Eq. (6).

§Calculated; from Tables 5 and 6.

‖Calculated from Eq. (4).

#Experimental; from Tables 5 and 6.

**$\Delta S^{\ddagger}$ and E calculated for α-hydrogen atoms only.

††Average for both types of H atoms.

‡‡Sum of two reaction paths.

This approach to calculating the energetics of a reaction is not novel: It relies on what is essentially a bond additivity argument. Heicklen[11] explored a similar approach to predicting BDEs, from which he predicted rate coefficients for reactions of OH radicals with a wide variety of organics. The difference here is the use of the approach directly for calculating activation energies, rather than BDEs. This shortcut circumvents the problem of the uncertainties in many BDEs--generally 1 to 2 kcal/mol--that may introduce errors into the bond additivity expressions for predicting unmeasured BDEs and hence in activation energies. Since the correlation factor in the equation relating activation energies with BDEs is approximately 0.4, a 2-kcal/mol error in BDE imparts an error to k(298) of a factor of 3.8.

A "UNIVERSAL" RATE COEFFICIENT EXPRESSION

Equation (6) for E(298)/R and Eq. (7) for $\Delta S^{\ddagger}(298)$ can be substituted in the general expression for k(T) from transition-state theory to yield a general rate coefficient expression for (OH + haloalkanes) that depends only on the molecular weight of the reagent and the number of various substituents. We can force a $T^{1.5}$ pre-exponential temperature dependence to agree with the results of the calculations shown in Tables 5 and 6. The A factor is determined by requiring the expression to yield the proper values of k(298) and E(298). The result is

$$k(T) = n_H \, 10^{6.5} \, M^{-1} \, T^{1.5} \exp(-B/T) \qquad (8)$$

where M is in daltons and T is in kelvins. We have modified the pre-exponential factors slightly to round off the exponent of the molecular weight factor M. The term B is calculated from E(298)/R obtained from Eq. (6) B = [E(298)/R - 450]. The rate coefficients resulting from Eq. (8) are shown for several typical (OH + haloalkane) reactions in Figs. 2 through 11. Calculated values of k(298) are tabulated in Table 7. Graphical results for other haloalkanes are given in Ref. 5. [Equation (8) does not apply to haloethanes with only β-hydrogens.] For $CH_2ClCHCl_2$ and CH_2FCHF_2, Eq. (8) was applied separately to the two different kinds of H atoms, and the results were summed together. The summed values are plotted in Figs. 7 and 8. In general, the rate coefficients calculated by Eq. (8) disagree with experimental data (where they exist) by less than a factor of 3.

Equation (8) differs from the analogous expression of Heicklen,[11] which is built on a much larger data base (OH with a wide variety of C-H-containing compounds), in three principal ways:

1. The exponential factor is based directly on experimental activation energies rather than BDEs. In practice, this should circumvent the additional inaccuracies introduced because of BDE uncertainties. In principle, the two approaches should differ negligibly--assuming the validity of the Evans-Polanyi-type correlation between activation energies and BDEs, which still seems to be a good assumption.

2. Heicklen's formulation suggests that k(T) is a constant for all H atoms of the same type in homologous molecules, a principle that past correlation schemes have relied upon as well. That is, if the C-H BDEs for secondary H atoms in C_3H_8 and $C_{30}H_{62}$ are the same, then k per H atom is the same for both molecules, and $k_s(C_{30}H_{62}) = 28k_s(C_3H_8)$, because the only dependence on molecular size is in the factor $\mu^{-0.5}$. For reagents of molecular weight significantly larger than that of OH, the reduced mass μ is essentially the mass of the OH, and hence is independent of reagent size. On the other hand, the results of the present study suggest that k(T) per H atom varies inversely with the molecular weight of the organic reagent. Formally, this comes about because as M increases, the changes in translational and rotational entropies upon forming the activated complex become progressively smaller. In the language of collision theory, the cross section of collision does not increase with molecular weight after the reagent is more than a few carbons long. The difference in predicted k(T) for the two formulations will be small for small molecules. Even for $C_{30}H_{62}$, k_s is only 10 times larger than $k_s(C_3H_8)$, or a factor of 3 smaller than Heicklen's prediction. Unfortunately, not enough data for such large molecules are available to permit testing which of the two formulations is the more accurate.

3. The temperature dependences of the two formulations are different. Heicklen's expression predicts a $T^{0.5}$ dependence, whereas this study predicts a $T^{1.5}$ dependence. The smaller T dependence is the limiting case for small molecules with no internal structure: It is the dependence predicted by simple collision theory. The $T^{1.5}$ dependence is what transition-state theory predicts in the limiting case of a nonlinear (polyatomic + diatomic) for which the activated complex has two new low-frequency modes and two free internal rotations. There is thus nothing surprising in Eq. (8). However, inasmuch as there are very few data above 500 K, there is no empirical basis at present for preferring the stronger temperature dependence of the present formulation, even though it has theoretical justification.

After most of this work was completed, another paper correlating rate coefficients for H-abstraction by OH radicals was published.[12] In it, the derived rate coefficient was expressed as a sum of contributions from various kinds of H atoms, depending on (1) whether there were 1, 2, or 3 H atoms attached to the carbon atom in question, and on (2) the nature of substituents attached to that carbon atom. For example, for the compound $CH_2FClCHCl_2$,

$$k(T) = k_s F(F)F(Cl) + k_t F(Cl)^2$$

where the k_s and k_t are universal rate coefficients for "secondary" and "tertiary" H atoms (i.e., H atoms attached to carbon atoms to which one, or no, other H atoms are attached, respectively); and the F(R) are correction factors of the form $\exp(E_R/T)$, one for each substituent on the carbon atom. The terms k_s, k_t, and k_p (the corresponding universal coefficient for "primary" H atoms) are given by equations of the form $[AT^2 \exp(E_i/T)]$. The resulting rate coefficients calculated with this formulation and the derived parameters fit quite well a large body of experimental data. Conceptually, this approach differs from that of this report in three ways:

1. It predicts a stronger pre-exponential temperature dependence (n = 2, rather than 1.5). In theory, the only way to get such a strong temperature dependence to the pre-exponential factor is to have at

least one hindered internal rotation with a fairly large potential barrier. In practice, the difference between $T^{1.5}$ and T^2 will be very small.

2. It assumes that k_p, k_s, and k_t can be reliably treated as constants. This in turn assumes that the entropy of activation is the same regardless of the size of the molecule from which the H atom is being abstracted. We have already discussed why we believe this is not strictly valid.

3. It assumes that the effect of a substituent is only on the activation energy, and not on the pre-exponential factor, which, in principle, is not valid. Consider, for example, CF_3CH_3 and CF_3CH_2Cl. The attack of the OH on the first of these will make a large change in the reduced moment of inertia for internal rotation, but only a small or negligible change on the second compound. This means a relatively larger entropy of activation for the first reaction, and a larger A factor. In practice, however, the effect may be lost in the experimental scatter.

REFERENCES

1. Jeong, K. M., and F. Kaufman. J. Phys. Chem., 86:1816, 1982; 88:1222, 1984.

2. Cohen, N. Int. J. Chem. Kinet., 14:1339, 1982; 15:503, 1983.

3. Cohen, N., and K. R. Westberg. Int. J. Chem. Kinet., 18:99, 1986.

4. Walch, S. P., and T. H. Dunning, Jr. J. Chem. Phys., 72:1303, 1980.

5. Cohen, N., and S. W. Benson. Transition-State Theory Calculations for Reactions of OH with Haloalkanes. I. Halomethanes. ATR-85(7072)-1, Vol. I. The Aerospace Corporation, El Segundo, California, 1985; Transition-State Theory Calculations for Reactions of OH with Haloalkanes. II. Haloethanes. ATR-85(7072)-1, Vol. II. The Aerospace Corporation, El Segundo, California, 1985.

6. Singleton, D. L., G. Paraskevopoulos, and R. S. Irwin. J. Phys. Chem., 84:2339, 1980.

7. Herschbach, D. R., H. S. Johnston, K. S. Pitzer, and R. F. Powell. J. Chem. Phys., 25:736, 1956.

8. Lewis, G. N., M. Randall, K. S. Pitzer, and L. Brewer. Thermodynamics, 2nd ed. McGraw-Hill, New York, 1961. Tables 27-8, 27-9, 27-12, and 27-13.

9. Davis, D. D., G. Machado, B. Conaway, Y. Oh, and R. Watson. J. Chem. Phys., 65:1268, 1976.

10. Howard, C. J., and K. M. Evenson. J. Chem. Phys., 64:197, 1976.

11. Heicklen, J. Int. J. Chem. Kinet., 13:651, 1981.

12. Atkinson, R. Int. J. Chem. Kinet., 18:555, 1986.

13. Howard, C. J., and K. M. Evenson. J. Chem. Phys., 64:4303, 1976.

14. Paraskevopoulos, G., D. L. Singleton, and R. S. Irwin. J. Phys. Chem., 85:561, 1981.

15. Handwerk, V., and R. Zellner. Ber. Bunsenges. Phys. Chem., 82:1161, 1978.

16. Nip, W. S., D. L. Singleton, R. Overend, and G. Paraskevopoulos. J. Phys. Chem., 83:2440, 1979.

17. Jeong, K. M., K. J. Hsu, J. B. Jeffries, and F. Kaufman. J. Phys. Chem., 88:1222, 1984.

18. Watson, R. T., A. R. Ravishankara, G. Machado, S. Wagner, and D. D. Davis. Int. J. Chem. Kinet., 11:187, 1979.

19. Jeong, K. M., and F. Kaufman. Geophys. Res. Lett., 6:757, 1979.

20. Clyne, M. A. A., and P. M. Holt. J. Chem. Soc. Faraday Trans. 2, 75:569, 582, 1979.

21. Martin, J. P., and G. Paraskevopoulos. Can. J. Chem., 61:861, 1983.

22. Kurylo, M. J., P. C. Anderson, and O. Klais. Geophys. Res. Lett., 6:760, 1979.

23. Watson, R. T., G. Machado, B. Conaway, S. Wagner, and D. D. Davis. J. Phys. Chem., 81:256, 1977.

24. Chang, J. S., and F. Kaufman. J. Chem. Phys., 66:4989, 1977.